

π -electron theory of transverse optical excitons in semiconducting single-walled carbon nanotubes

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We present a quantitative theory of optical absorption polarized transverse to the tube axes in semiconducting single-walled carbon nanotubes. Within one-electron theory, transverse optical absorption occurs at an energy that is exactly in the middle of the two lowest longitudinal absorption energies. For nonzero Coulomb interactions between the π -electrons, transverse optical absorption is to an exciton state that is strongly blueshifted relative to the longitudinal excitons. Very similar behavior is observed in the π -conjugated polymer poly-paraphenylenevinylene, where the optical absorption polarized predominantly perpendicular to the polymer chain axis is blueshifted relative to the absorptions polarized predominantly along the chain axis. The binding energy of the transverse exciton in the nanotubes is considerably smaller than those of the longitudinal excitons. Electron-electron interactions also reduce the relative oscillator strength of the transverse optical absorption. Our theoretical results are in excellent agreement with recent experimental measurements in four chiral nanotubes.

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I. INTRODUCTION

It is now firmly established that optical absorptions polarized parallel to the nanotube axes in semiconducting single-walled carbon nanotubes (SWNTs) are to exciton states.^{1,2,3,4,5,6,7,8,9,10} Theoretical work by different groups have established that in the subspace of excited states that are coupled to the ground state by the longitudinal component of the dipole operator, there occur a series of energy manifolds (labeled by an index $n = 1, 2, \dots$ etc.), with each energy manifold containing optical and dark excitons, and a continuum band separated from the optical exciton by a characteristic exciton binding energy. Nonlinear spectroscopic measurements have been applied to determine the binding energy of the $n = 1$ longitudinal exciton (hereafter Ex1) in a number of SWNTs.^{11,12,13,14} The determination of the binding energy of the $n = 2$ exciton (hereafter Ex2) appears to be more difficult within the existing experimental approaches. Recent theoretical works have suggested that electroabsorption may be a useful tool for this purpose.^{15,16}

In contrast to the longitudinal absorption, the literature on optical absorptions polarized transverse to the nanotube axes, theoretical^{1,4,6,8,17} as well as experimental,^{18,19} is rather limited. Early theoretical investigations had largely emphasized the suppression of the perpendicularly polarized absorption due to local field effects.^{1,4,6} Later work based on π -electron theory⁸ found nonzero oscillator strength for the transverse absorption. More interestingly, while within the noninteracting nearest neighbor (nn) tight-binding model the transverse absorption is expected at the exact middle of the lowest two longitudinal absorptions, inclusion of the Coulomb interactions between the π -electrons leads to a splitting of the final states to which transverse absorption occurs: to a redshifted forbidden state and a blueshifted allowed state.⁸ Correlated electron calculation for the

(8,0) SWNT found the allowed transverse absorption relatively far from Ex1 occurring at energy E_{11} and very close to Ex2 occurring at E_{22} .⁸ Significant blueshift of the transverse absorption has also been found more recently within an effective mass approximation theory.¹⁷

Experimentally, excited states coupled to the ground state by the transverse component of the dipole operator have recently been detected by polarized photoluminescence excitation (PLE) spectroscopy.^{18,19} Miyauchi *et al.* have determined the PL spectra for four chiral SWNTs with diameters $d = 0.75 - 0.9$ nm.¹⁸ In all cases, the allowed transverse optical absorption is close to E_{22} , in agreement with theoretical prediction.⁸ Lefebvre and Finnie have detected transverse absorptions close to E_{22} in 25 SWNTs with even larger diameters,¹⁹ and were also able to demonstrate the same “family behavior” in transverse absorption energies that had been noted previously with longitudinal absorptions.²⁰

There is general agreement between the different research groups that the extent of the blueshift of the transverse absorption is a direct measure of the strength of the Coulomb electron-electron (e-e) interactions in SWNTs.^{8,17,18,19} Indeed this blueshift is much more easily determined (provided the states are observable experimentally) than other correlation-induced energy splittings such as exciton binding energies or the energy differences between the optical and dark excitons within any longitudinal manifold. We have recently demonstrated that the Coulomb interaction parameters obtained by fitting the absorption spectra in the π -conjugated polymer poly-paraphenylenevinylene (PPV)²¹ can reproduce quantitatively the energies of Ex1, Ex2 and the corresponding two-photon excitons in SWNTs with diameters $d \geq 0.75$ nm.^{14,22} Here we report detailed calculations of the transverse absorption for the four SWNTs that have been investigated by Miyauchi *et al.*,¹⁸ (6,5), (7,5), (7,6) and (8,4), within the same model π -electron

Hamiltonian with the same e-e and one-electron parameters. Our goal is to establish the model Hamiltonian and the parameters firmly for SWNTs. In addition, we point out the remarkable parallels between the present discussions and earlier ones focusing on optical absorption polarized perpendicular to the polymer chain axis in PPV^{21,23,24,25,26,27,28,29,30}. Comparisons between PPV and SWNTs allow us to make the effects of e-e interactions clearer.

II. THEORETICAL MODEL, PARAMETRIZATION AND BOUNDARY CONDITION

Our calculations are within the π -electron Pariser-Parr-Pople (PPP) model Hamiltonian,³²

$$\begin{aligned} H &= H_{1e} + H_{ee}, \\ H_{1e} &= - \sum_{i \neq j, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}), \\ H_{ee} &= U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} V_{ij} (n_i - 1)(n_j - 1). \end{aligned} \quad (1)$$

Here H_{1e} and H_{ee} consist of one-electron and many-electron interactions; $c_{i\sigma}^\dagger$ creates a π -electron with spin σ on the i th carbon atom, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the number of π -electrons with spin σ on the atom i , and $n_i = \sum_\sigma n_{i\sigma}$ is the total number of π -electrons on the atom. The parameters t_{ij} are the one-electron hopping integrals, U is the repulsion between two π -electrons occupying the same carbon atom, and V_{ij} the intersite Coulomb interactions. In our previous work^{8,14,22} we had limited the electron hopping to nn t_1 only; here we investigate the consequences of including next nearest neighbor (nnn) hopping t_2 , to determine the effects of broken charge-conjugation symmetry (CCS). Miyauchi *et al.*¹⁸ have tentatively ascribed a splitting observed in the transverse absorption bands of SWNTs to broken CCS; we examine this issue theoretically. Our choice of the Coulomb parameters, hereafter referred to as screened Ohno parameters,²¹ and the $t_1 = 2.0$ eV, are the same as in the case of longitudinal excitations.²² We use the single configuration interaction (SCI) approximation, which involves solving the Hamiltonian of Eq. (1) within the subspace of one electron-one hole excitations from the Hartree Fock ground state. The justification for this approximation has been given in our previous work.^{8,14,22} Our calculations are for open boundary condition, which enables precise determinations of transition dipole moments.^{8,14,22} The number of unit cells we retain are 5 – 6 for the (6,5), (7,5) and (7,6) SWNTs, and 22 for the (8,4) SWNT, with 2100 – 2500 carbon atoms in all cases. Convergence in the calculated energies as well as excellent agreement with experiment are seen at these system sizes for the $n = 1$ and 2 longitudinal optical excitons.²²

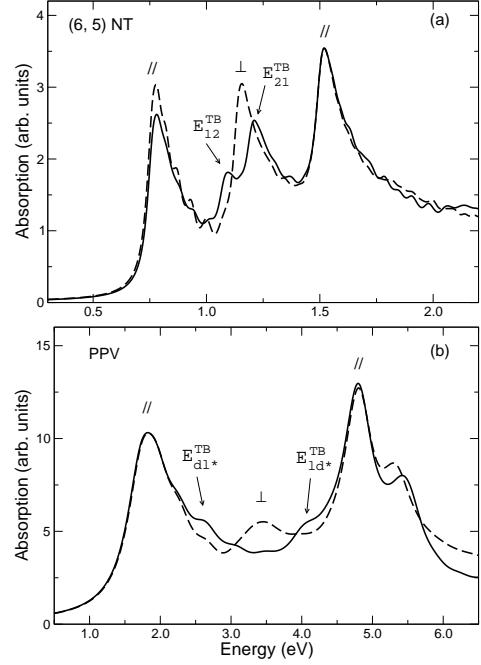


FIG. 1: Calculated optical absorption spectra of (a) a (6,5) SWNT, and (b) PPV within the tight binding model for $t_2 = 0$ (dashed line) and $t_2 = 0.6$ eV (solid line). The longitudinal (//) and transverse (perp) components of the optical absorption are indicated in each case.

III. RESULTS AND DISCUSSION

A. One-electron tight-binding limit

In view of what follows we begin with a discussion of the $U = V_{ij} = 0$ tight binding (TB) limit of Eq. (1) for both SWNTs and PPV. Transverse absorption in SWNTs is due to the optically induced transitions from the highest valence subband v_1 to the second lowest conduction subband c_2 , and from the second highest valence band v_2 to the lowest conduction band c_1 (see Fig. 2 in Ref. 8). We denote the one-electron excitations as $\psi_{v1 \rightarrow c_2}$ and $\psi_{v2 \rightarrow c_1}$, respectively, and the corresponding excitation energies as E_{12}^{TB} and E_{21}^{TB} . The two transitions are degenerate for $t_2 = 0$, and occur exactly at the center of the two longitudinal transitions E_{11}^{TB} and E_{22}^{TB} . This is shown in Fig. 1(a) for the (6,5) SWNT, for $t_1 = 2.0$ eV. The nn only TB band structure of PPV is similar (see Fig. 1 in Ref. 33), although the nomenclature is different. The equivalents of v_2 and c_2 are localized flat bands which are labeled l and l^* , respectively, while the delocalized equivalents of v_1 and c_1 are labeled d and d^* , respectively. Once again the degenerate transverse transitions $d \rightarrow l^*$ and $l \rightarrow d^*$ occur exactly at the center of the longitudinal $d \rightarrow d^*$ and $l \rightarrow l^*$ transitions, as is shown in Fig. 1(b) for $t_1 = 2.4$ eV, which is appropriate for planar π -conjugated systems. The oscillator strength of the central peak, relative to those for the longitudinal transitions, is much larger in the SWNT than in PPV.

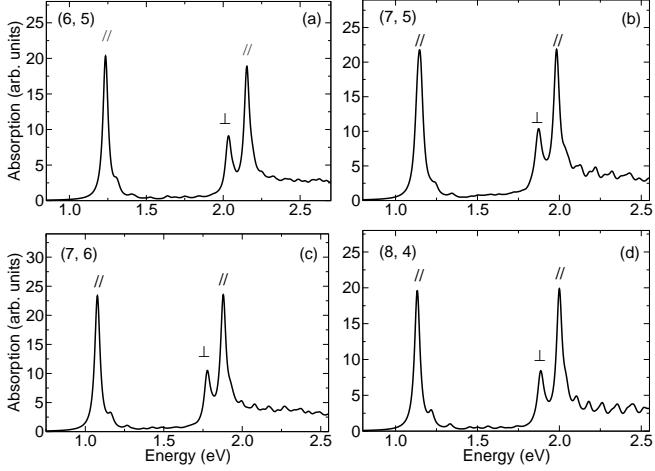


FIG. 2: Calculated optical absorption spectra within the PPP model, with $t_1 = 2.0$ eV, $t_2 = 0$, for four chiral SWNTs. The longitudinal and transverse components of the absorption are indicated in each case.

This is a reflection of the larger electron-hole separation that is possible in the transverse direction in a SWNT with $d \sim 1$ nm, as compared to PPV.

The degeneracy between E_{12}^{TB} and E_{21}^{TB} (E_{dl}^{TB} and E_{ld}^{TB} in PPV) is lost if CCS is broken by including t_2 . Fig. 1 shows the effect of $t_2 = 0.6$ eV on the absorption spectra of the (6,5) SWNT and PPV; we will argue below that this is the largest possible nnn hopping between π -orbitals. The splitting between the transverse transitions is much smaller in the (6,5) SWNT than in PPV. We have found this to be true for all four SWNTs we have studied. We do not show results of including a third-neighbor hopping, since this does not contribute any further to the splitting of the transverse states.

B. Nonzero e-e interaction

We now discuss the full PPP Hamiltonian of Eq. (1). The matrix element $\langle \psi_{v1 \rightarrow c2} | H_{ee} | \psi_{c1 \rightarrow v2} \rangle$ is nonzero, and as a consequence eigenstates of the Hamiltonian are now odd and even superpositions of these basis functions, $\Psi_O = \psi_{v1 \rightarrow c2} - \psi_{c1 \rightarrow v2}$ and $\Psi_E = \psi_{v1 \rightarrow c2} + \psi_{c1 \rightarrow v2}$. Repulsive H_{ee} ensures that the optically forbidden Ψ_O is redshifted while the optically allowed Ψ_E is blueshifted. The mechanism of the above energy splitting into bright and dark states is identical to that behind the splitting of the longitudinal excitons into bright and dark excitons⁸, with the only difference that the magnitude of the splitting in the present case is much larger (see below). This strong first order configuration interaction effect occurs over and above the overall blueshift of the entire absorption spectrum due to e-e interactions; as a consequence the allowed transverse exciton Ψ_E is blueshifted also with respect to the longitudinal excitons. In Fig. 2 we have shown our calculated optical absorption spectra within

Eq. (1) for $t_1 = 2.0$ eV, $t_2 = 0$, for all four SWNTs investigated by Miyauchi *et al.*¹⁸ In all cases the optically allowed transverse exciton is seen to occur very close to the $n = 2$ exciton, as observed experimentally.¹⁸ The relative oscillator strength of the transverse exciton is now considerably weaker than Ex1 and Ex2.

The mechanism of the splitting of the degenerate transverse excitations is identical to that in PPV, where also the optically allowed $d \rightarrow l^* + l \rightarrow d^*$ transverse excitation occurs closer to the $l \rightarrow l^*$ exciton than to the $d \rightarrow d^*$ exciton.^{21,23,28,29,30} We emphasize that the coupling between $\psi_{v1 \rightarrow c2}$ and $\psi_{c1 \rightarrow v2}$ is independent of the boundary condition (periodic versus open) along the longitudinal direction: the calculations for PPV in references 28 and 29, for example, employ periodic boundary condition. In the present case, we have repeated our calculations of all energies and wavefunctions, but not transition dipole couplings (which is difficult to define with periodic boundary condition within tight-binding models³¹), for all four SWNTs also with periodic boundary condition. In every case we have confirmed the splitting of the transverse wavefunctions into Ψ_O and Ψ_E from wavefunction analysis. We have confirmed that the energy differences between the odd and even superpositions the same with the two boundary conditions, for the number of unit cells used in the calculation. Our parametrization of the V_{ij} involves a dielectric constant^{8,22}. The energy splitting between the odd and even superpositions will occur for any finite dielectric constant, and only the magnitude of the splitting depends on the value of the dielectric constant.

We have previously shown that the screened Ohno Coulomb parameters along with $t_1 = 2.0$ eV and $t_2 = 0$ reproduce the experimental E_{11} and E_{22} of the four SWNTs of interest quantitatively. The difference between the experimental and calculated E_{11} is 0.02 – 0.06 eV, while the same for E_{22} is about twice these values (see Table II in Ref 22). In Fig. 3 we make quantitative comparisons between the experimental transverse optical absorption spectra of Miyauchi *et al.*¹⁸ with those calculated within Eq. (1) for both $t_2 = 0$ and $t_2 = 0.6$ eV. As seen in Fig. 1, E_{11} and E_{22} in SWNTs are unaffected by t_2 even for $H_{ee} = 0$, so that our fits to these²² continue to be valid. The low frequency regions of the experimental spectra are dominated by background noise and are therefore ignored in our discussions below.

We compare experimental and calculated transverse optical absorptions of the SWNTs in Fig. 3. The peak heights of the calculated absorption spectra in Fig. 3 have been adjusted to match those of the experimental spectra. The experimental absorption spectra show two peaks with nearly the same separation in all cases, ~ 0.1 eV. Independent of which of these two peaks correspond to the true electronic energy of Ψ_E , it is clear that the error in our calculation is again small, ≤ 0.1 eV. The experimental transverse absorption bands are much broader than the longitudinal absorption bands in all cases, a feature that is qualitatively reproduced in our calculated spec-

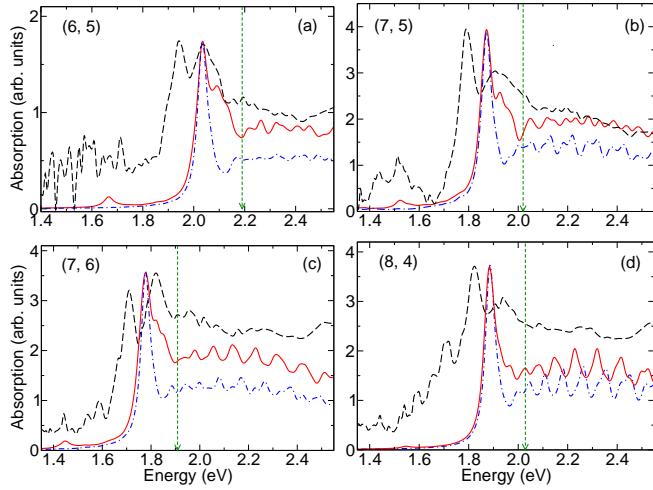


FIG. 3: (Color online) Comparison of experimental¹⁸ (dashed curves) and calculated transverse components of optical absorptions in four SWNTs for $t_2 = 0$ (dot-dashed curves) and $t_2 = 0.6$ eV (solid curves). The vertical lines correspond to the Hartree–Fock threshold.

tra. This is a consequence of the much smaller binding energy of the transverse exciton, which leads to incomplete transfer of oscillator strength from the continuum band to the exciton. Binding energies of longitudinal excitons are larger and there occur greater transfer of oscillator strength from the corresponding continua to the excitons.^{18,34} The broad absorption beyond the excitons in Fig. 3 are therefore to continuum band states. We have indicated in Fig. 3 the Hartree-Fock thresholds for the transverse states, which is the lower edge of the continuum band within the SCI approximation. The binding energies of the transverse excitons, taken as the difference between the Hartree-Fock threshold and the exciton energy, are ~ 0.15 eV for all four SWNTs, which is about one-third of that of the $n = 1$ longitudinal exciton. Miyauchi *et al.*, from a different perspective, have also arrived at the conclusion that the binding energy of the transverse exciton is small.¹⁸ Similar conclusion was reached in PPV from photoconductivity studies.²⁷

We now discuss the energy splitting of ~ 0.1 eV between the peaks in the experimental absorption spectra. Miyauchi *et al.* ascribe this to broken CCS, viz., non-degenerate E_{12}^{TB} and E_{21}^{TB} even within H_{1e} . Our calculated absorption spectra in Fig. 3 for t_2 as large as 0.6 eV, nearly one-third of t_1 , however, fail to reproduce this splitting. This is to be anticipated from the $H_{ee} = 0$ absorption spectrum of Fig. 1(a), since any splitting due to broken CCS, a one-electron effect, can only be smaller for $H_{ee} \neq 0$. At the same time, $t_2 = 0.6$ eV should be considered as the upper limit for the nnn electron hopping based on experiments in PPV as we explain below.

The experimental absorption spectra of PPV-derivatives resemble *qualitatively* the tight-binding absorption spectrum of Fig. 1(b) for $t_2 \neq 0$, with, however, an overall blueshift due to e-e interactions. The

spectra contain strong absorption bands at $\sim 2.2 - 2.4$ eV and 6 eV, and weaker features at 3.7 eV and 4.7 eV, respectively. The lowest and highest absorption bands are polarized predominantly along the polymer chain axis, while the 4.7 eV band is polarized perpendicular to the chain axis^{23,24,25,26}. It is then tempting, based on Fig. 1(b), to ascribe the origin of the 3.7 eV band to broken CCS, in which case it ought to have the same polarization as the 4.7 eV absorption band. Repeated experiments have, however, found that the absorption band at 3.7 eV to be polarized predominantly along the polymer chain axis.^{23,24,25,26} Theoretical calculations within the PPP model with $t_2 = 0$ have reproduced the longitudinal polarization of the 3.7 eV band, which is ascribed to the second lowest longitudinal exciton in PPV derivatives.^{21,23,30} We have confirmed that inclusion of $t_2 = 0.6$ eV within the same PPP model calculation renders the polarization of the 3.7 eV absorption band perpendicular to the polymer chain direction (not shown), in contradiction to experiments. The nnn hopping in PPV is therefore certainly smaller than 0.6 eV. Curvature of SWNTs implies an even smaller value in SWNTs.²² We are consequently unable to give a satisfactory explanation of the splitting in the transverse absorption in SWNTs. We have not found any higher energy transverse exciton whose oscillator strength can explain the observed absorption spectra. It is conceivable that the second peak in the experimental absorption spectra in Fig. 3 correspond to the threshold of the transverse continuum band (see in particular the spectra in Figs. 3(b) and (d)). Further experimental work is therefore warranted. It is also possible that the energy splitting is due to higher order correlation effects neglected in SCI, or due to intertube interactions. We are currently investigating the latter possibilities.

IV. CONCLUSION

In conclusion, eigenstates coupled to the ground state by the transverse component of the dipole operator are degenerate within one-electron theory in both SWNTs and PPV. $H_{ee} \neq 0$ splits this degeneracy, and the optically allowed higher energy state appears close to the higher energy longitudinal excitons in SWNTs. The binding energies of the transverse excitons are about one-third of those of the longitudinal excitons. The quantitative aspect of our calculations is worthy of note. We have now demonstrated that the same model Hamiltonian with the same one-electron hopping and Coulomb interactions can reproduce the experimental energies and absorption spectra of longitudinal and transverse optical excitations in SWNTs with diameters greater than 0.75 nm with considerable precision (errors $\leq 0.05 - 0.1$ eV). In those cases where the experimental binding energies of Ex1 are known, the calculated quantities are uniformly very close.²² It has been suggested that the true single tube binding energies are considerably larger than the

0.3 – 0.4 eV that are found experimentally^{11,12,13,14} for SWNTs with diameters ~ 0.75 – 1 nm, and the experimental quantities reflect strong screening of e-e interactions by the environment. The close agreements between our theoretical single tube calculations and experiments suggest, however, that any such environment effect on the exciton binding energy is small.

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